



AFRL-RX-WP-TP-2011-4064

**SYNTHESIS AND CRYSTAL STRUCTURE OF
(BENZOTRITHIOPHENE)₂(TCNQ) A POSSIBLE ONE-
DIMENSIONAL THERMOELECTRIC MATERIAL
(BRIEFING CHARTS)**

Sampe 2010

Joel Schmidt, Dougls Dudis, and Albert Fratini

**Thermal Sciences and Materials Branch
Nonmetallic Materials Division**

MAY 2010

Interim

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UNITED STATES AIR FORCE**

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14. ABSTRACT Quasi-one-dimensional (Q1D) organic crystals may offer good thermoelectric properties. Thermoelectric efficiencies twenty times greater than current thermoelectric materials have been predicted for Q1D materials. This theoretical prediction shows the potential that this new class of materials has to revolutionize electrical generation as well as cooling since thermoelectric devices operate with no moving parts and have a very long service life. Q1D materials are formed from parallel stacks of molecules. One Q1D material is benzo[1,2-c:3,4-c':5,6-c'']trithiophene (BTT) which has been previously synthesized and characterized. BTT was doped with 7,7,8,8-tertacyano-p-quinodimethane (TCNQ) in order to improve the material's semiconductive properties, to hopefully retain the material's Q1D behavior, and yield improved thermoelectric parameters. TCNQ is an electron acceptor well known to form charge transfer compounds which also exhibits a Q1D molecular structure. A single crystal structure analysis was performed to determine the molecular packing of the new BTT/TCNQ complex.					
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Synthesis and Crystal Structure of (Benzotrithiophene)₂(TCNQ) a Possible One-Dimensional Thermoelectric Material



SAMPE 2010
Seattle, WA
May 18, 2010

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Materials and Manufacturing Directorate
Air Force Research Laboratory



Thermoelectric Materials



- Durable solid state devices which provide cooling, power generation and waste heat harvesting
- Used on deep space probes, sensor cooling and small scale refrigeration
- Figure-of-Merit

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$

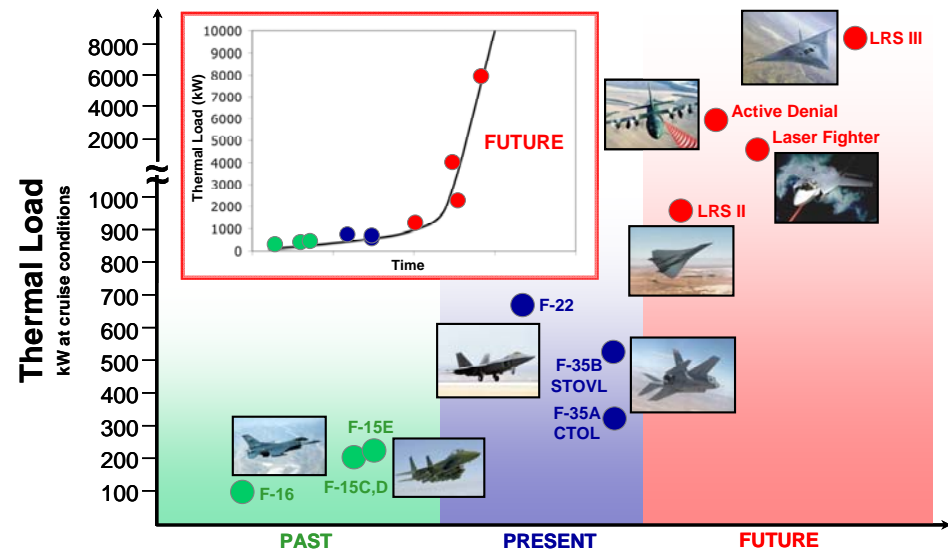
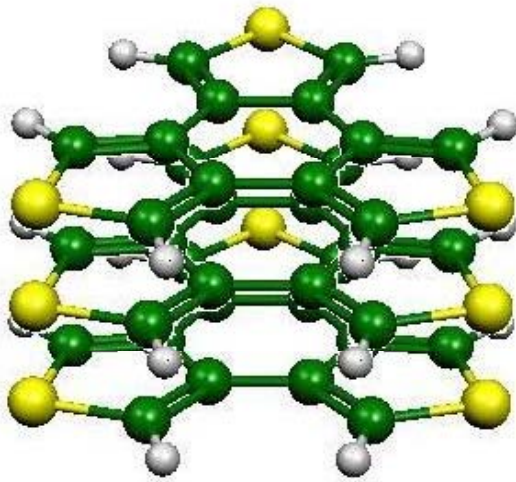
- Current $ZT \approx 1$ (10% of Carnot efficiency)
- $ZT = 2-4$ competitive with current refrigeration
- $ZT = 20$ predicted for Q1D materials



Material Requirements



- Optimized thermoelectric parameters
- Novel material approach
- Handle increasing thermal loads
- Temperature stability
- Quasi-One Dimensional



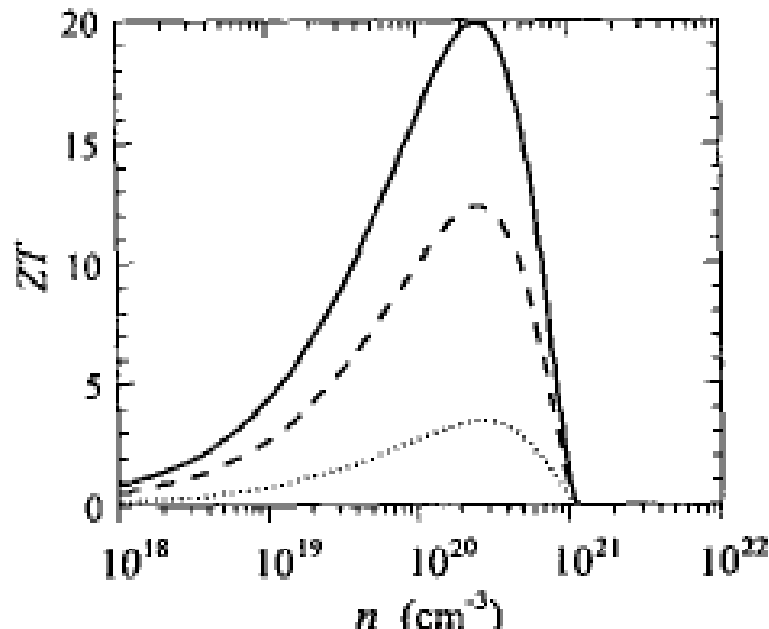
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Quasi-One-Dimensional Materials

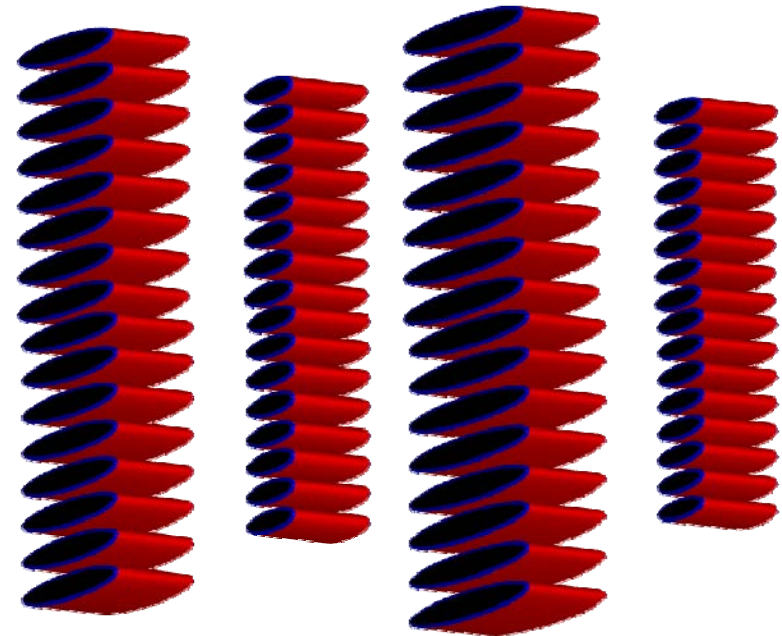


- Good electrical conductivity along the chains
- Thermal conductivity limited in the stacking direction



A Possibility to Realize a High Thermoelectric Figure of Merit in Quasi-One-Dimensional Organic Crystals

A. Casian, Z. Dashevsky, H. Scherrer, V. Duscic, and R. Duscic
22nd International Conference on Thermoelectrics



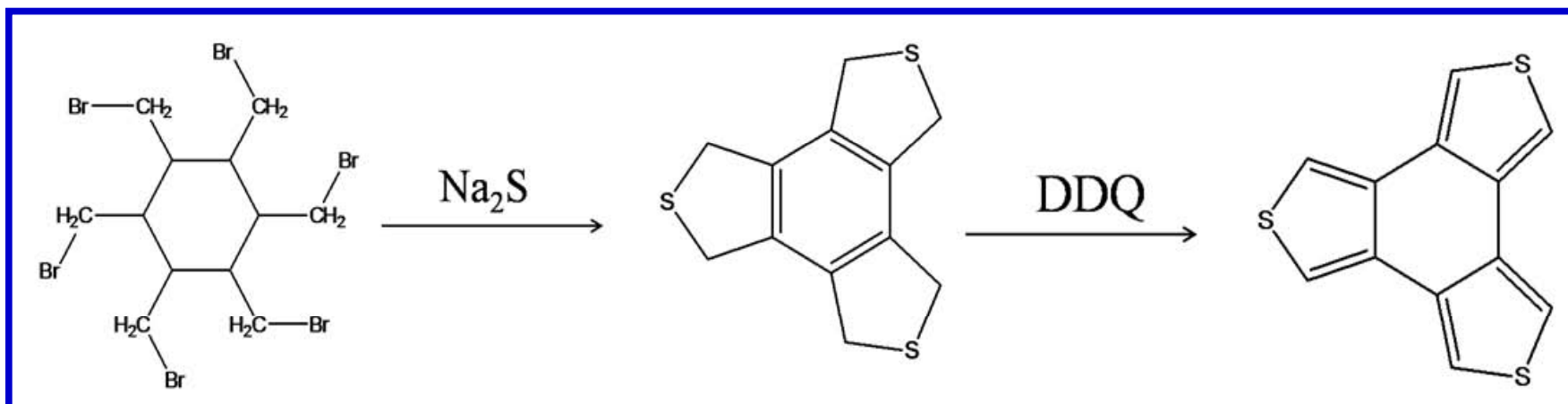
- University of Moldova studies found $ZT=20$ possible for Q1D material with optimized charge carrier concentration



Benzotrithiophene

- Prepared using literature preparation

– Hart, H. & Sasaoka, M. *J. Am. Chem. Soc.* 100 (1978): 4326-4327.



Purification Procedure

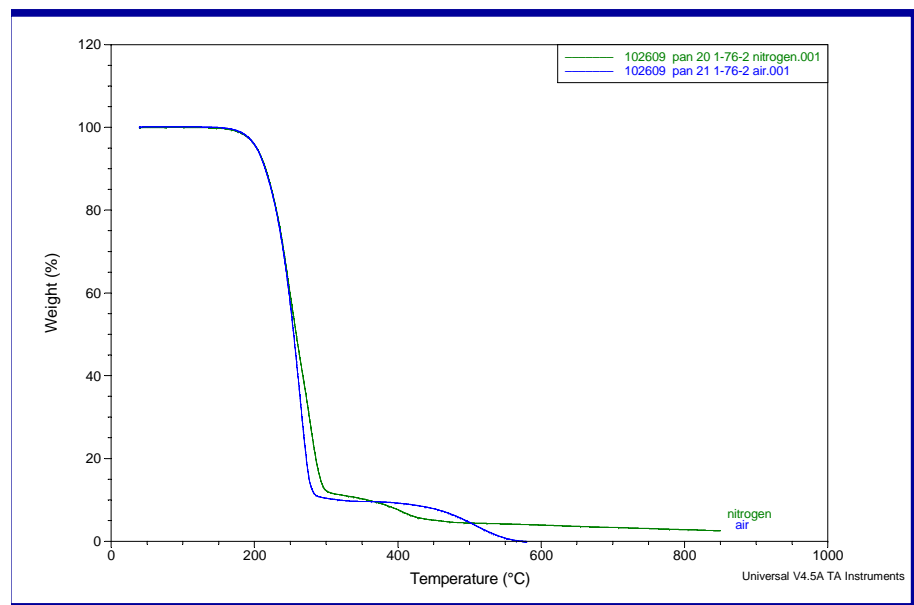
Column Chromatography → Sublimation → Recrystallization



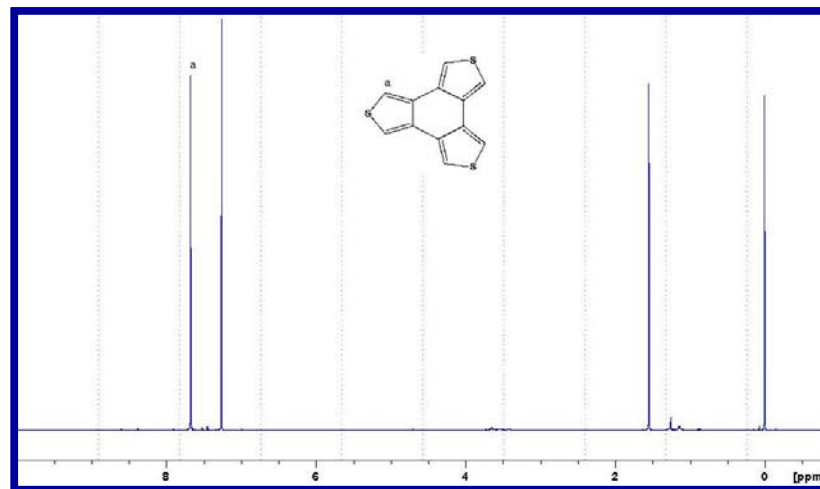
Benzotrithiophene



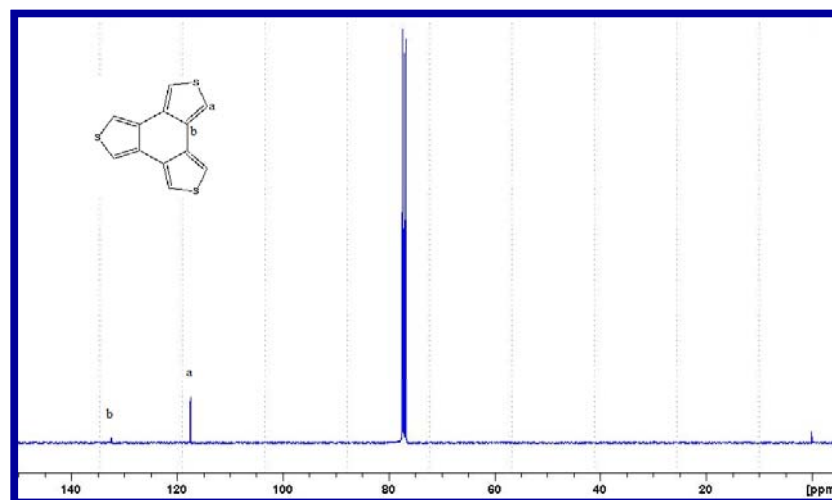
- Purity
- Thermal Stability
 - MP > 200 C



TGA



¹H NMR



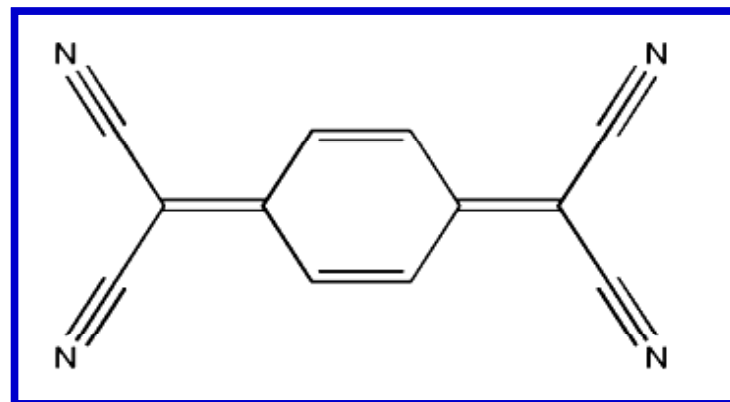
¹³C NMR



TCNQ Doping



- Well known electron acceptor
- Forms a Q1D complex with TTF
- Hart and Sasaoka report a BTT-TCNQ complex but no characterization
- Doping conducted in chlorobenzene/acetonitrile mixture





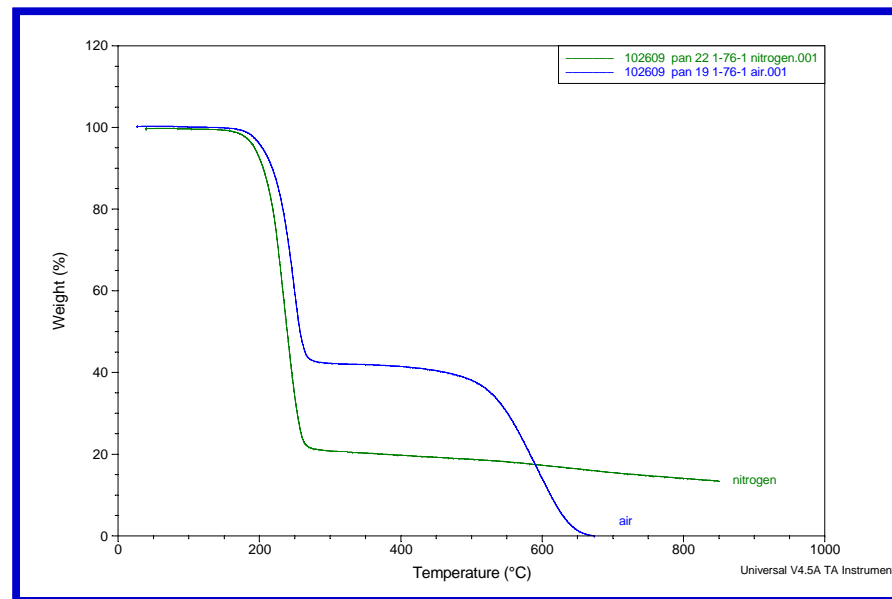
Characterization



- **Elemental analysis of bulk material**

Element	Theoretical	Experimental
Carbon	62.04%	62.90
Hydrogen	2.32%	2.44%
Nitrogen	8.04%	10.06%
Sulfur	27.60%	25.26%

- **TGA of bulk material**

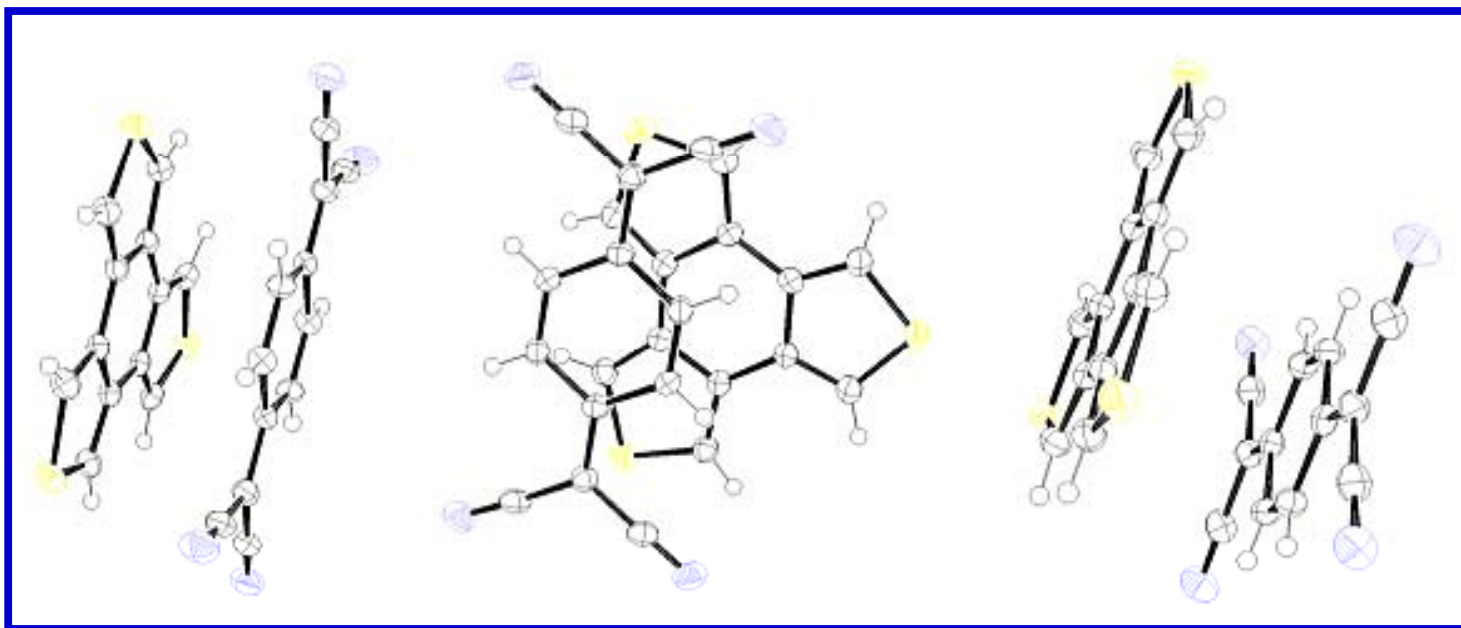


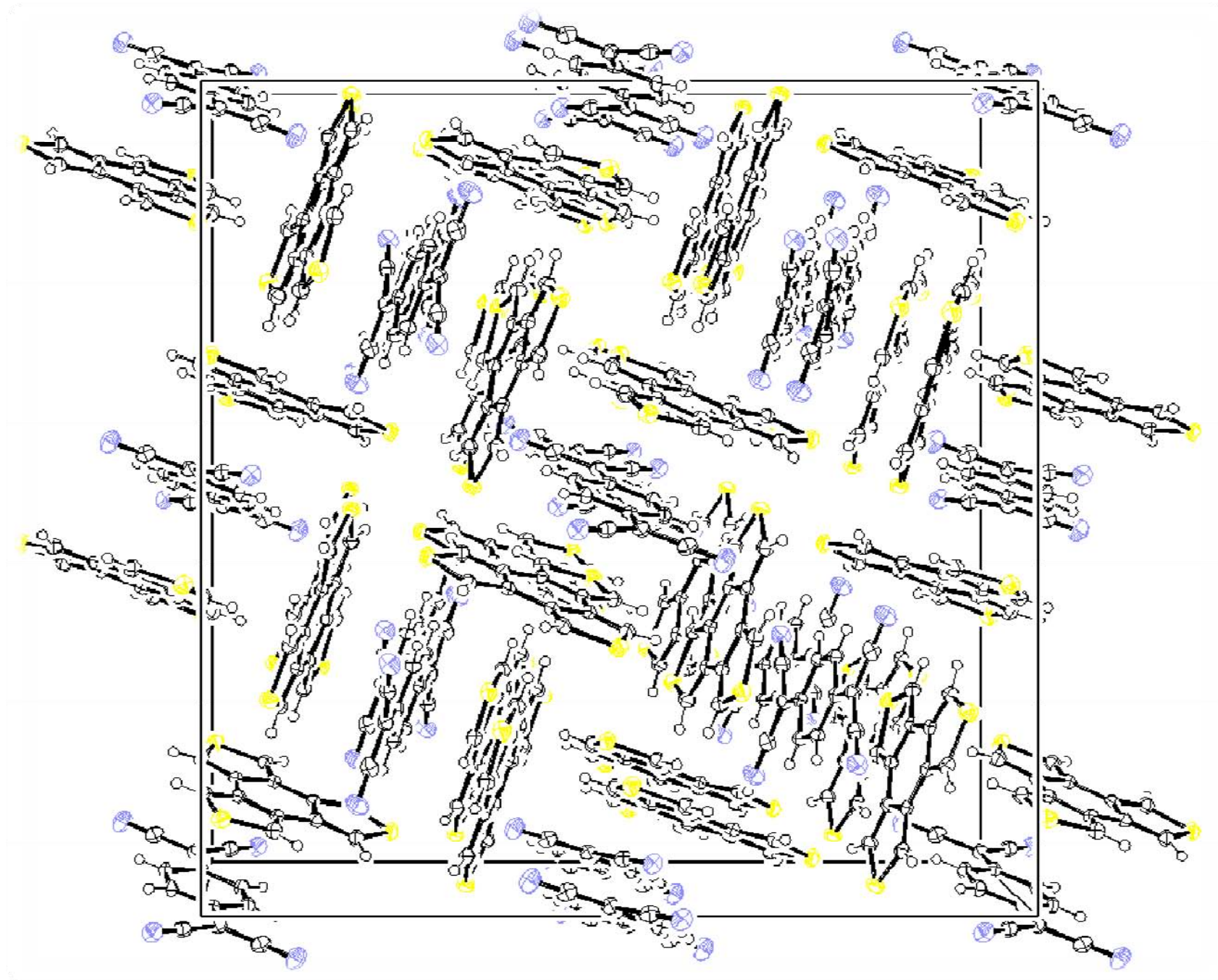


Single Crystal Analysis



- $I4_1/a$ tetragonal structure with a stoichiometry of $(\text{BTT})_2(\text{TCNQ})$
- Cell dimensions $24.6 \text{ \AA} \times 24.6 \text{ \AA} \times 10.5 \text{ \AA}$
- Packing in alternating BTT-TCNQ-BTT triads



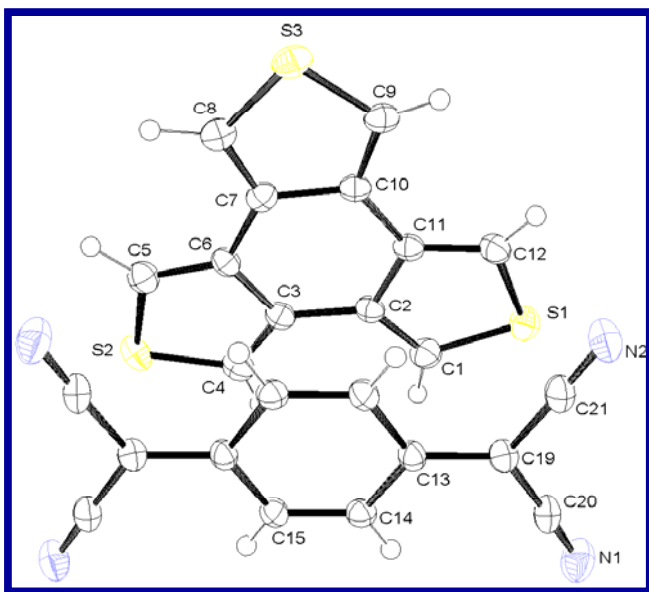




Material Evaluation



- Packing structure is BTT-TCNQ-BTT triads
- Triads are not oriented in same direction
- Good electrical properties are not expected
- Material is not Q1D in nature

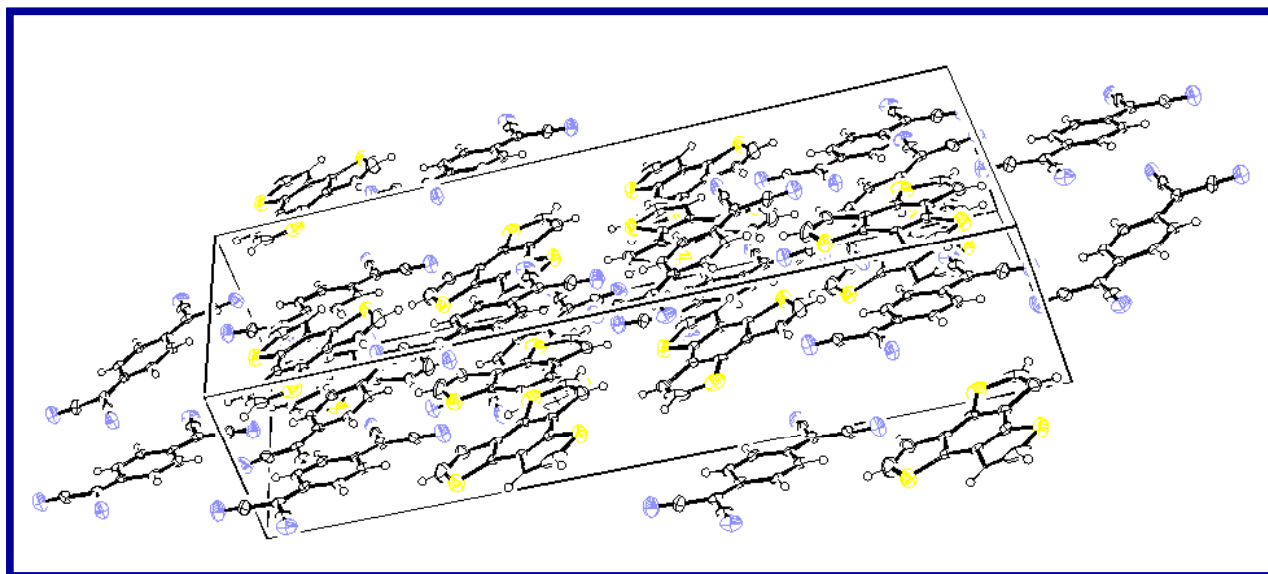
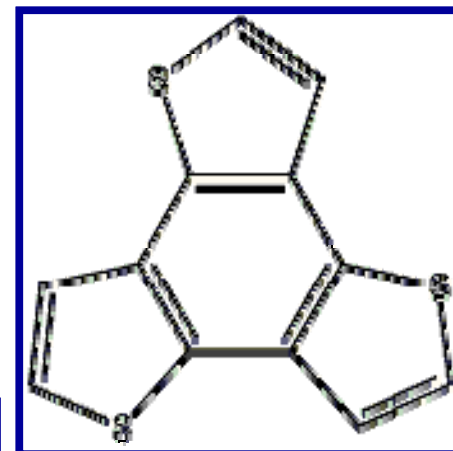




Future Work



- **Electrical conductivity measurements**
- **Dope other isomer of BTT with TCNQ**
 - Benzo[1,2-c:3,4-c':5,6-c'']trithiophene (BTT2)
- **Preliminary Structure**





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